

## DECON GREEN

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Simple solutions of hydrogen peroxide, carbonate/bicarbonate, and co-solvents afford the rapid, broad-spectrum decontamination of chemical warfare agents. Such formulations, termed “DECON GREEN”, are non-toxic, non-corrosive and environmentally friendly. Reactivity arises from in situ generated peroxy anion  $\text{OOH}^-$  and peroxocarbonate  $\text{HCO}_4^-$ , which, respectively, afford the rapid perhydrolysis of VX and GD to their non-toxic phosphonic acids, and the oxidation of HD to its non-vesicant sulfoxide. DECON GREEN performs well at decontaminating CARC painted panels.

## INTRODUCTION

The U.S. Army is developing environmentally friendly decontamination systems to replace current, problematic decontaminants such as hypochlorite.<sup>1</sup> Desirable characteristics for the replacement include maintaining a broad-spectrum reactivity towards all agents, even in cold weather operations, while achieving a significant reduction in the toxic, corrosive and environmentally harmful nature of the decontaminant. Decontaminants such as hypochlorite are corrosive and produce undesirable reaction products for HD which retain irritant and/or vesicant properties.<sup>1</sup>

In industrial applications, environmental concerns have been driving the replacement of chlorine based bleaching processes with peroxide based systems.<sup>2</sup> These “green” peroxide systems avoid the formation of toxic, carcinogenic chlorinated organic compounds such as those produced in paper production.<sup>3</sup> Peroxide based systems may also be employed in *military* applications, replacing historical chlorine based “bleach” decontaminants. Such systems afford the necessary rapid reactions and, as in the case of industrial bleaching, avoid undesirable products. We call this fledgling, but promising decontamination system “DECON GREEN.” In this paper, the reaction chemistry and kinetics of agents in DECON GREEN formulations will be discussed, and results for the performance of DECON GREEN at decontaminating painted panels will be presented.

## EXPERIMENTAL

Aqueous 30 and 50 wt % hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), urea hydrogen peroxide addition compound ( $\text{NH}_2\text{C}(\text{O})\text{NH}_2 \cdot \text{H}_2\text{O}_2$ , 98 % pure, 36 wt %  $\text{H}_2\text{O}_2$ ), polypropylene glycol (PPG-425, avg. MW 425) and other solvents were obtained from Aldrich. Decon solutions were mixed by first dissolving bicarbonate

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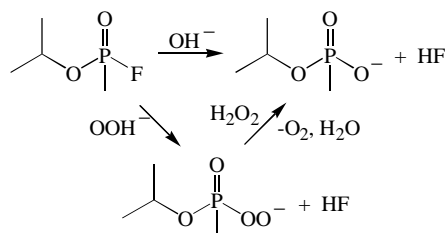
and/or carbonate in the aqueous  $\text{H}_2\text{O}_2$  prior to adding the co-solvents. Urea hydrogen peroxide and  $\text{NaHCO}_3$  were simultaneously dissolved in water before adding the co-solvent. Reactions of GB, GD, VX and HD with decon solutions were monitored by  $^{31}\text{P}$  and  $^1\text{H}$  NMR using a Varian Unityplus 300 NMR spectrometer. Spectra were referenced to external 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ , 0 ppm) and TMS ( $^1\text{H}$ , 0 ppm). Reactions were initiated by adding neat GB, GD, VX and HD to the decon solution contained in a 5 mm NMR tube. The tubes were capped, wrapped with parafilm and shaken to thoroughly mix the contents. **Caution:** These experiments should only be performed by trained personnel using applicable safety procedures. Final concentrations of 0.01M GB, GD and VX, and 0.1M HD were used.

Chemical Agent Resistant Coating (CARC) painted coupons were contaminated with several 2  $\mu\text{L}$  drops of VX, TGD, or HD to obtain a challenge of 1  $\text{mg}/\text{cm}^2$  (10  $\text{g}/\text{m}^2$ ). The panels were allowed to stand for 1 h, at which point sufficient decon solution was applied to just cover the panel. The decon solution was allowed to act for 30 min before being removed with a water rinse. The panel was then allowed to briefly dry in air before being immersed in chloroform for 1 h to extract residual agent. The agent extracts were assayed by a Hewlett-Packard 5890 GC.

## RESULTS AND DISCUSSION

Basic peroxide has been known to rapidly decontaminate GB (Sarin) for decades,<sup>4</sup> via generation of the powerful nucleophile peroxy anion  $\text{OOH}^-$ . This reaction is shown in Scheme 1. We have observed the long-suspected<sup>4</sup> peroxyphosphonate intermediate using  $^{31}\text{P}$  NMR for both GB and GD, which yield peaks at 42.2 and 41.6, 41.0 ppm (two diastereomers), respectively. Representative reactions for GB and GD are shown in Table 1. GB in neutral peroxide exhibits an initial half-life of 67 h, apparently reacting with background  $\text{OOH}^-$ . But the reaction quickly slows prior to completion as the pH and  $[\text{OOH}^-]$  drop. However, with even small amounts of bicarbonate the reactions for both GB and GD become too fast to measure by NMR ( $t_{1/2} \ll 1$  min) and go to completion. Although perhydrolysis is indeed fast, G agents are also easily decontaminated by dilute alkali,<sup>1</sup> so peroxide offers limited advantage for these agents.

SCHEME 1



Quite recently, however, it was found that VX also undergoes rapid perhydrolysis to selectively yield ethyl methyphosphonic acid (EMPA) as shown in Scheme 2.<sup>5</sup> The *N*-oxide of VX (VX-NO) also forms; similarly undergoing perhydrolysis, but at a slower rate. No peroxy-EMPA intermediate is observed, perhaps owing to immediate reaction with liberated thiolate.<sup>5</sup> Unlike the G agents, perhydrolysis is a much more effective decontamination reaction for VX as toxic EA-2192 is avoided.<sup>5</sup> Basic hydrolysis yields about 22% EA-2192.<sup>6</sup> Representative reactions for VX are shown in Table 1. In neutral peroxide, some autocatalytic behavior is evident owing to protonation of the VX amine group with concomitant generation of  $\text{OOH}^-$ . However, formation of acidic products lowers the pH such that the reaction stops prior to completion and no further perhydrolysis or hydrolysis occurs over the course of

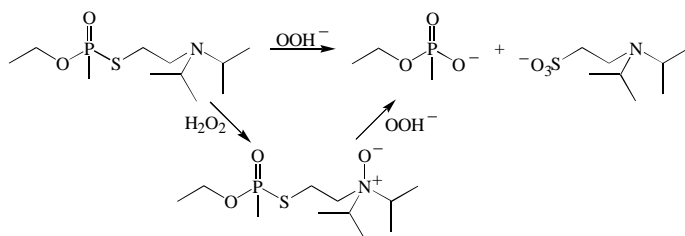
several hours. But with the addition of bicarbonate, the additional buffering capacity drives the reaction to completion.

TABLE 1. Half-Lives Observed for VX, GB and HD.

No.	Activators	Peroxide	Co-Solvents	$t_{1/2}$			
				VX	GB	HD	HDO
1	None	1.3 ml 30% $\text{H}_2\text{O}_2^a$	1.9 ml t-BuOH	$>>16 \text{ h}^{b,c}$	29 days	42 min	
2	0.037 M $\text{NaHCO}_3$	1.3 ml 30% $\text{H}_2\text{O}_2^a$	1.9 ml t-BuOH	120 min <sup>c</sup>	$<1 \text{ min}^d$	20 min <sup>e</sup>	
3	0.1 M $\text{NaHCO}_3$	1.3 ml 50% $\text{H}_2\text{O}_2^f$	1.9 ml t-BuOH	11 min <sup>c</sup>	$<1 \text{ min}^d$	2.1 min	
4	“	“	1.9 ml EtOH		-	-	1.8
5	“	“	1.9 ml i-PrOH		-	-	1.8
6	“	“	1.9 ml PPG-425		-	-	1.9
7	0.33 M $\text{NaHCO}_3$	1.0 ml 50% $\text{H}_2\text{O}_2^g$	1.0 ml t-BuOH	56 sec <sup>c</sup>	-	-	
8	0.75 M $\text{NaHCO}_3$	0.743g urea- $\text{H}_2\text{O}_2^h$ in 1 ml $\text{H}_2\text{O}$	1.0 ml t-BuOH	7.5 min <sup>c</sup>	$<1 \text{ min}^d$	1.6 min	
9	0.2 M $\text{KHCO}_3$	0.5 ml 50% $\text{H}_2\text{O}_2^i$	0.2 ml i-PrOH + 0.3 ml Triton X-100	2.6 min <sup>c</sup>	-	2.1 min	245 h
10	0.1M $\text{KHCO}_3$ + 0.1M $\text{K}_2\text{CO}_3$	“	“	$<1 \text{ min}^{c,d}$	-	2.4 min	40 h

<sup>a</sup>Final solution contains 15 wt%  $\text{H}_2\text{O}_2$ . <sup>b</sup>About 50% VX/VX-NO reacted within 1 h, but no further reaction occurred after 16 h. <sup>c</sup>Includes decay of slower-reacting VX-NO. <sup>d</sup>Reaction too fast to measure. <sup>e</sup>From reference 13a. <sup>f</sup>22 to 26 wt%  $\text{H}_2\text{O}_2$ , depending on the density of the alcohol. <sup>g</sup>30 wt%  $\text{H}_2\text{O}_2$ . <sup>h</sup>11 wt%  $\text{H}_2\text{O}_2$ . <sup>i</sup>28 wt%  $\text{H}_2\text{O}_2$ .

## SCHEME 2



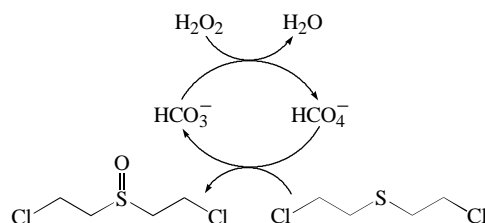
Although HD may be decontaminated by hydrolysis to non-toxic thiodiglycol,<sup>1</sup> its nucleophilic substitution is quite slow, proceeding exclusively via S<sub>N</sub>1.<sup>7</sup> On the other hand, the oxidation of HD to the sulfoxide and sulfone can be extremely rapid.<sup>1,8</sup> As to the suitability of the sulfoxide and sulfone as decontamination products, relevant properties<sup>9-11</sup> are shown in Table 2. The sulfoxide is non-vesicant<sup>9,10</sup> and quite stable towards hydrolysis.<sup>9</sup> However, it should be noted that the sulfoxide does retain a subcutaneous toxicity identical to HD.<sup>9</sup> The sulfone retains both appreciable vesicant activity<sup>9,10</sup> and subcutaneous/intravenous toxicity,<sup>9,11</sup> but does undergo slow hydrolysis.<sup>9</sup> Thus HD may be rendered non-vesicant via selective oxidation to the sulfoxide. And, if formed, the sulfone is water-soluble and thus more amenable to hydrolysis than HD itself. Although powerful oxidants such as hypochlorite and peroxyacids (i.e. *m*-chloroperoxybenzoic acid) effect rapid oxidation of HD, they are rather non-selective, simultaneously producing both sulfoxide and sulfone. The milder oxidant hydrogen peroxide selectively yields the sulfoxide, but the reaction is too slow for the purpose of immediate decontamination. As shown in Table 1, HD is oxidized fairly slowly in only peroxide and co-solvent. Yet, ironically, this reaction is much faster than those observed for comparable amounts of VX and GD under the same conditions. Recently it has been shown that the activator bicarbonate<sup>12,13</sup> is able to effect the rapid oxidation of sulfides and HD catalytically. In peroxide, bicarbonate forms peroxocarbonate HCO<sub>4</sub><sup>-</sup> which selectively oxidizes sulfides and HD to their corresponding sulfoxides.<sup>12,13</sup> This reaction is shown for HD in Scheme 3. [HCO<sub>4</sub><sup>-</sup>] is maximized near pH 7 and goes to zero near pH 11.<sup>14</sup> However, in the pH vicinity required for effective GB and VX hydrolysis (pH 8 to 9, see above), sufficient HCO<sub>4</sub><sup>-</sup> remains to quickly oxidize HD with a half-life of less than 2 min. The last two entries in Table 1 show that HD sulfoxide (HDO) is subject to further oxidation to the sulfone (HDO<sub>2</sub>), but the rate of this undesirable reaction is orders of magnitude slower than the oxidation of HD itself.

TABLE 2. Toxic Properties of HD, HDO and HDO<sub>2</sub>.

	Toxicity (mouse, mg/kg)	Vesicant Action	Relative Hydrolysis Rate
HD	125 <sup>a</sup> ; 8.6 <sup>b</sup>	most irritating <sup>c</sup> ; severe <sup>d</sup>	Fast (50% in 10 min, 20°C) <sup>c</sup>
HDO	125 <sup>a</sup>	scarcely irritating <sup>c</sup> ; none <sup>d</sup>	Not hydrolyzed, even at 100°C <sup>c</sup>
HDO <sub>2</sub>	105 <sup>a</sup> ; 50 <sup>b</sup>	slightly less than HD <sup>c</sup> ; severe <sup>d</sup>	Slow (55.9% in 150 min, 22°C) <sup>c</sup>

<sup>a</sup>Subcutaneous, reference 10. <sup>b</sup>Intravenous, reference 12. <sup>c</sup>Reference 10. <sup>d</sup>Reference 11.

### SCHEME 3



Thus a simple solution of hydrogen peroxide, bicarbonate, and a suitable co-solvent for water-insoluble HD achieves the desired broad-spectrum, rapid decontamination of all three types of agents.<sup>12b</sup> It

is interesting to note that with the use of edible co-solvents such as EtOH or PPG-425 (a food additive) the decontamination of GB, VX, and HD can be accomplished using *only* food-grade materials! The environmental advantages of such formulations are self-evident. Further note that solid urea peroxide addition compound (urea-H<sub>2</sub>O<sub>2</sub>) may be substituted for aqueous peroxide as this material yields solutions of the correct pH. Other common solid peroxides yield pH's that are either too high (e.g. sodium percarbonate, pH 10.5<sup>15</sup>) or too low (potassium peroxomonosulfate, pH 2-3<sup>15</sup>). Additionally, urea peroxide possesses the highest active oxygen content of the solid peroxides, though still less than that of aqueous 50% H<sub>2</sub>O<sub>2</sub>.

Although the above solutions are quite adept at decontaminating VX, GB, GD, and HD in agitated, homogenous solution, decontamination of agents and thickened agents on surfaces is more challenging. Results for the decontamination of VX, thickened GD (TGD), and HD on Chemical Agent Resistant Coating (CARC) painted panels using select DECON GREEN formulations are shown in Table 3.

TABLE 3. Decontamination of CARC Panels.

No.	Solvents/Peroxide (Vol%)	Activators	% Agent Decontaminated <sup>a</sup>		
			VX	TGD	HD
1	Diacetone Alcohol (52.5) Sulfolane (22.5) 50% H <sub>2</sub> O <sub>2</sub> (23) Triton X-100 (2)	0.1M KHCO <sub>3</sub> 0.1M K <sub>2</sub> CO <sub>3</sub>	95.91%	99.66%	-
2	Propylene Carbonate (75) 50% H <sub>2</sub> O <sub>2</sub> (23) Triton X-100 (2)	Same	96.66%	99.95%	-
3	Diacetone Alcohol (44) Sulfolane (19) 50% H <sub>2</sub> O <sub>2</sub> (36) Triton X-100 (1)	Same	-	-	87.55%
4	Propylene Carbonate (62.5) 50% H <sub>2</sub> O <sub>2</sub> (36.5) Triton X-100 (1)	Same	-	-	97.20%

<sup>a</sup>Initial contamination level 1000 µg-cm<sup>-2</sup>. <sup>b</sup>Average of three runs.

The various DECON GREEN formulations signify a promising decontamination efficacy. However, to achieve this feat inedible, but non-toxic industrial co-solvents are required; primarily to dissolve TGD. In the case of VX and HD, significant amounts of agent remain, and this is attributed to sorption or swelling of these agents into the paint itself during the hour-long residence time. In this regard, thickened agents are actually *easier* to decontaminate since they do not sorb readily into surfaces. Work is continuing to examine the decontamination of agent sorbed within paint.

## CONCLUSIONS

The fast, effective decontamination of GB, VX, TGD, and HD using activated hydrogen peroxide and suitable co-solvents has been demonstrated. For non-thickened agents, decontamination may be realized using only innocuous food-grade materials. Inedible, but non-toxic solvents allow the decontamination of thickened agents from surfaces. These latter formulations of DECON GREEN perform well in the decontamination of CARC painted panels.

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